I. SEPARATION OF ORGANIC ACIDS BY CHROMATOGRAPHY

II. POLYMERIZATION AND STRUCTURE OF CATIONIC POLYBUTADIENE

BY

ROBERT DELAFIELD RANDS, JR.

B.S., University of Maryland, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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PART I

SEPARATION OF ORGANIC ACIDS BY CHROMATOGRAPHY

Introduction

In connection with the problem of the structure of diene polymers the need has been encountered for a rapid and efficient method for the separation of organic acids. It was also desirable that the method be as quantitative as possible to allow an accurate reconstruction of the polymer chain. Previously, fractional distillation of methyl esters (1) and fractional extraction (2) were used with some success, but these methods have serious limitations.

It was the purpose of this investigation to explore the methods of chromatography in the solution of the problem.

Discussion Of Results

A partition chromatography procedure was developed which allowed an almost complete resolution of the water-soluble acids from the oxidation of diene polymers. The immobile phase consisted of water adsorbed on silicic acid. The mobile phase was continually increased in polarity during the separation by using an increasing ratio of *n*-butanol to chloroform.

The procedure was found to be generally applicable for the separation of water-soluble organic acids. Mixtures containing acids of such closely related structures as *o*-, *m*-, and *p*-hydroxybenzoic, malic and tartaric, or adipic, glutaric, succinic, malonic, and oxalic were easily separated. The threshold volumes of thirty-six acids were determined.

An adsorption chromatographic method was developed for the separation of the water-insoluble acids from the oxidation of styrene-butadiene copolymers.

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PART II

POLYMERIZATION AND STRUCTURE OF CATIONIC POLYBUTADIENE

Introduction

The poymerization of Butyl rubber, which is carried out at low temperatures in the presence of a Friedel-Crafts catalyst, is very rapid and yields a high-molecular weight, essentially linear, polymer. It was one of the purposes of this investigation to discover whether a useful rubber-like polymer could be prepared in a similar manner with butadiene alone. It was also of interest to compare the structure of cationic polybutadiene with emulsion polybutadiene.

Discussion Of Results

The etherate as well as the hydrate of boron fluoride was found to catalyze the polymerization of butadiene at temperatures beteween — 20 and 50° C. but not at — 75° C. The polymers formed were low molecular weight and tended to be highly cross-linked as indicated by their low solubilities. The effect of catalyst concentration, time of polymerization, conversion, and dilution were determined, but the results were somewhat obscured by a lack of reproducibility. Trace amounts of water had a pronounced effect on the course of the polymerization causing increased conversions.

For structure studies it was necessary to develop a method of oxidizing insoluble polymers. Oxidation with *t*-butylhydro-

peroxide and osmium tetroxide was not as satisfactory as an ozonization procedure in which alternate ozonization and hydrogen peroxide cleavage were used.

The acids obtained from ozonization of cationic polybutadiene were resolved by the partition chromatography method described in Part I and compared with the acids from ozonization of emulsion polybutadiene.

VITA

The author was born in Buitenzorg, Java, Netherlands East Indies, on October 17, 1919. He attended the public schools of Washington, D.C., graduating from Roosevelt High School in June, 1938. In September of that year he enrolled at the University of Wisconsin. The following September he transferred to the University of Maryland from which he received a Bachelor of Science degree in chemistry in June, 1942.

For three years the author was employed as a physical chemist at the National Bureau of Standards. He was inducted into the United States Army in July, 1945, and served a year on the Manhattan Project at Oak Ridge, Tennessee. After his army discharge in August, 1946, he enrolled in the Graduate School at the Uinversity of Illinois where, from the spring of 1947 until the fall of 1949, he was employed as a research assistant on the Rubber Reserve program.